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COMPLETE SPECIFICATION

Organic-Silica Aerogels, their production and use

We, MONSANTO COMPANY (formerly known as Monsanto Chemical Company), a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis, 66, State of Missouri, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel organo-silica aerogels, to sols for the production of such aerogels, and to processes for preparing such aerogels and sols.

The organo-silica aerogels of the invention have properties, of surface area, pore size and thixotropic capacity, which render them particularly useful as thickening agents, and the invention accordingly includes thickened compositions obtained by their use.

It has been proposed in United States patent No. 2,093,454 to produce silica aerogels by precipitating colloidal silica in a liquid as a gel, washing the gel with water to remove an appreciable amount of inorganic metal salts present therein, replacing the water in the gel with a lower boiling water miscible liquid such as ethanol, confining the resultant gel in an autoclave and heating the gel until the liquid in the gel has reached a temperature at which the surface tension of the liquid is so small as to produce no substantial shrinkage of the gel when the vapor is allowed to escape. The vapor is then slowly released from the autoclave so as not to impair the internal structure of the gel. In this way the skeleton structure of the gel is preserved approximately in its original porous state and the product is a light fluffy solid having void spaces up to 99% and higher.

It has also been proposed in United States patent No. 2,285,449 to prepare inorganic aerogels such as silica aerogels by first forming an aquasol containing a dissolved inorganic alkali metal salt and a colloidal inorganic oxide such as colloidal silica, adding to the aquasol a quantity of a water-miscible organic solvent such as ethanol to precipitate such salt, removing a substantial portion of the precipitated inorganic alkali metal salt from the resulting hydro-organosol and removing the liquid phase, which consists of water and an organic solvent, (e.g. ethanol), from the sol without substantially subjecting the sol to a compressive liquid-solid interface. The silica aerogels, prepared as described in these patents contain some alkali metal cations and are characterized in having a highly porous structure, a specific surface area of between 100 and 250 square meters per gram, and are readily ground or comminuted to particles or aggregates having an average particle size of from 5 to 9 microns, which particles have an external surface area of generally less than 0.5 square meters per gram. Although it is possible to reduce further the particle size of such aerogels, such reduction can only be accomplished by extensive grinding or comminuting (which is expensive) and results in a relatively small decrease in particle size and a concomitant small increase in external surface area, such external surface area being below 0.7 square meters per gram.

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Such silica aerogels have been widely used as insulating materials, as reinforcing agents or fillers in silicon rubber formulations and as flattening agents in paint and varnish formulations. However, the utility of the aforescribed silica aerogels as reinforcing agents in liquid polymerizable materials or liquid thermosetting polymers such as, for example, polyester and epoxide polymers is limited due to the relatively inefficient thickening properties of these aerogels. Thus, in order to secure a desirable thickening of uncured polymers, a relatively large amount, e.g. up to 12% by weight of such aerogels, is required to obtain adequate thickening whereas amounts of thickening agents employed in excess of 4% by weight of the polymers usually adversely affect the properties of such polymers when cured. Also, the relative inefficiency of these aerogels as thickening agents limits their use in polymerizable surface coating materials, such as paints and varnish, where a thixotropic state is desired to prevent the flow and run-off of the coating materials after their application to a particular surface.

In accordance with the present invention there are provided organo-silica aerogels which have many of the advantages of the silica aerogels described in the prior literature, and which, in addition, have excellent thickening properties when incorporated in organic liquids and thus do not have the aforementioned disadvantage inherent in previously known silica aerogels.

According to a first feature of the present invention therefore, there are provided novel, amorphous organo-silica aerogels comprising a silica polymer having siloxy groups and containing carbon and hydrogen atoms chemically bound to a portion of the siloxy groups in said aerogel, said aerogel having an SiO₂ to carbon atom ratio of from 10:1 to 50:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 2:1. Differently stated, the organo-silica aerogels of this invention usually contain in chemically combined form in the aerogel, from 0.4% to 1.2% by weight of carbon and from 0.9% to 1.5% by weight of hydrogen. The preferred organo-silica aerogels of this invention are further characterized in having a total surface area of from 100 to 400 square meters per gram, most preferably 250 to 350 square meters per gram. The novel organo-silica aerogels of this invention which are particularly preferred have the aforementioned characteristics and, in addition, have at least one or all of the following characteristics: (a) a total pore volume of from 600 to 800 milliliters per gram, (b) an average pore radius of between 100 and 200 angstroms, (c) an average particle size in the range of from 1.0 to 2.5 microns, (d) a particle size distribution in the range of from 0.5 to slightly less than 6.0 microns and (e) an external surface area of from 1.70 to 1.95 square meters per gram.

The present invention provides two distinct, but inter-related classes of amorphous organo-silica aerogels having at least the SiO₂ to carbon atom and hydrogen atom ratios and specific surface areas within the ranges described in the preceding paragraph. However the two classes of organo-silica aerogels differ from each other with respect to chemical composition and, as will be evident hereinafter, with respect to their ability to thicken certain classes of organic liquids.

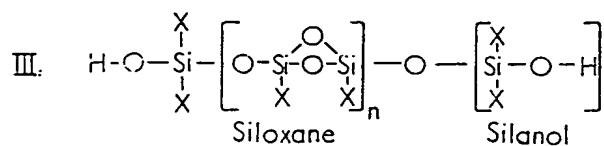
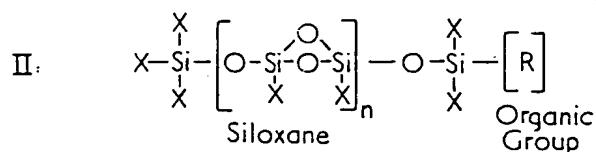
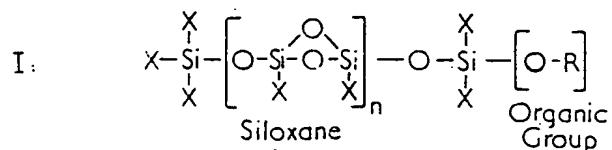
One preferred class of the amorphous organo-silica aerogels of this invention hereinafter designated as Group I organo-silica aerogels, comprise a silica polymer having siloxy groups and containing carbon and hydrogen atoms chemically bound to a portion of the siloxy groups in the aerogel and are further characterized in having an SiO₂ to carbon atom ratio of from 10:1 to 25:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 1.3:1. Stated differently, the Group I organo-silica aerogels of this invention contain from 0.9% to 1.2% by weight of carbon and from 1.2% to 1.5% by weight of hydrogen.

Another preferred class of the amorphous organo-silica aerogels of the present invention, hereinafter designated as Group II organo-silica aerogels, comprise a silica polymer having siloxy groups and containing carbon and hydrogen atoms chemically bound to a portion of the siloxy groups in the aerogel and are characterized in having an SiO₂ to carbon atom ratio of from 25:1 to 50:1 and an SiO₂ to hydrogen atom ratio of from 1.3:1 to 2:1. Stated differently the Group II organo-silica aerogels contain from 0.4% to 0.8% by weight of carbon and from 0.9% to 1.2% by weight of hydrogen.

The present invention also provides novel, amorphous finely divided organo-silica aerogels of the aforementioned classes having the above described chemical compositions and physical properties, and which, preferably, have an external surface area of from 1.7 to 1.95 square meters per gram and an average particle size in the range of from 1.0 to 2.5 microns. Such finely divided organo-silica aerogels are preferably composed of particles having a particle size distribution in the range of 0.5 to

slightly less than 6.0 microns. The particle size distribution of the particles of the finely divided organo-silica aerogels of this invention is preferably such that from 20% to 30% of the particles have a particle size of between 0.5 and 1.0 microns, 20% to 30% of the particles have a particle size in the range of 1.0 to 2.0 microns, 40% to 60% of the particles have a particle size in the range of 2.0 to 4.0 microns, and from 3% to 8% of the particles have a particle size greater than 4.0 microns, but less than 6.0 microns.

As stated hereinbefore the novel amorphous organo-silica aerogels of this invention are characterized in having carbon and hydrogen atoms bound to a portion of the siloxy groups in the aerogel. Although it is not known with certainty how the carbon atoms are bound to the siloxy groups it is believed that the following general types of chemical bondings exist at least to some extent in the organo-silica aerogels.



In formulae I and II, R is an organic group or radical, usually a hydrocarbon group, and, preferably an alkyl group such as, for example, a methyl, ethyl or a propyl group, and X may represent a silica polymer, an organo-substituted silica polymer, an organic group as represented in formulae I and II, or a silanol group as represented in formula III. In these formulae "n" is a whole number greater than 1.

The novel amorphous organo-silica aerogels of the present invention may be prepared by a process which comprises heating silica aerogels, prepared from certain hereinafter described silica hydro-organosols, at a temperature and for a time sufficient to form organo-silica aerogels having the chemical composition and physical properties hereinbefore described. The heating temperature employed may vary, but will generally depend, as will be hereinafter evident, upon the particular organo-silica aerogel which it is desired to prepare. In general, temperatures in the range of 90°C to 750°C may be used in most instances. The heating time may vary from a few seconds to several hours, and in general, will depend on the temperature used, but is also dependent upon the particular organo-silica aerogel which it is desired to obtain. Generally speaking, shorter heating times are employed when higher temperature are utilized.

One preferred class of novel organo-silica aerogels of this invention, hereinbefore described as Group I organo-silica aerogels, may be prepared by a process which comprises heating the starting silica aerogels at a temperature in the range of from 90°C to 375°C, preferably 250°C to 375°C, until an organo-silica aerogel having the chemical composition and physical properties of the Group I organo-silica aerogels, is formed. The heating times employed may vary widely and are generally in the range of from 3 seconds to several minutes and are usually in the range of from 3 to 50 seconds when the preferred temperatures, e.g. 250°C to 375°C are employed. Generally speaking, the shorter heating times will correspond to the higher temperatures used. When temperatures below 90°C are employed the heating times are usually unduly prolonged and, moreover, a product resembling the starting silica aerogels is usually obtained. When temperatures above 375°C are employed a product resembling the Group II organo-silica aerogels is usually obtained.

Another preferred class of organo-silica aerogels of this invention, that is, the Group II organo-silica aerogels, may be prepared by a process which comprises heating a starting silica aerogel at a temperature in the range of from 350°C to 750°C, preferably from 600°C to 700°C, until an organo-silica aerogel having the chemical composition and physical properties of the Group II organo-silica aerogels is formed. The heating times employed may vary to some extent depending upon the temperature employed, but are usually in the range of from about 15 seconds to 2 hours, the shorter heating times corresponding to the higher temperatures. When temperatures within the preferred ranges, e.g. 600°C to 700°C, are employed the heating time is usually from 30 to 90 seconds. When temperatures below 350°C are employed the product obtained will usually resemble the Group I organo-silica aerogels. On the other hand, when temperatures above 750°C are used the product generally contains a substantially smaller amount of the carbon and hydrogen than the carbon and hydrogen present in the Group II organo-silica aerogels. Alternatively the Group II organo-silica aerogels may also be prepared by heating the Group I organo-silica aerogels under the above described time and higher temperature conditions.

Although the novel silica aerogels of this invention may be prepared by the processes hereinbefore described, it has been found both desirable and advantageous, in order to obtain optimum benefits and optimum aerogel properties, to heat the starting silica aerogels within the aforementioned ranges of time and temperature at a pressure in the range of from 10 psig to 200 psig preferably a pressure of from 100 to 200 psig. The heating under pressure may be carried out in an atmosphere of an inert gas such as, for example, nitrogen or steam within the above described temperature time and pressure ranges. In the preparation of the Group I organo-silica aerogels it has been found particularly advantageous to heat the starting silica aerogels in an atmosphere of superheated steam at a pressure of from about 100 psig to about 200 psig. In the preparation of the Group II aerogels which are prepared either from starting silica aerogels or from Group I organo-silica aerogels, the heating is usually most advantageously carried out in air either at atmospheric pressure or at the elevated pressure ranges above described and at the temperatures and times hereinbefore described for the preparation of the Group II aerogels.

The novel finely divided amorphous organo-silica aerogels of this invention may be prepared by comminuting or grinding the starting silica aerogels prior to, during or after heating such aerogels under the above described conditions. Simultaneous heating and comminuting or grinding is the preferred procedure.

The starting silica aerogels which can be employed in producing the novel silica aerogels of this invention may advantageously be prepared from certain hereinafter described acidic silica hydro-organosols. Thus, such acidic silica hydro-organosols may be prepared using a procedure somewhat similar to that described in United States patent No. 2,285,477 or the processes described in United States patent No. 2,285,449 provided such procedure or processes are suitably modified. The processes of United States patent No. 2,285,477 comprise first forming an acidic silica aquasol having a pH between 1.8 and 4.5, by acidifying a water-soluble alkali silicate such as sodium silicate with a mineral acid such as sulfuric acid in the proper proportions. This sol, which is an aquasol, is cooled to cause precipitation of the salt formed by the reaction of the silicate and sulfuric acid, and the precipitated salt is removed from the sol. The process also provides for the addition of about 0.5% to 25% by weight of the sol of a water-miscible organic liquid, such as ethanol, prior to cooling to facilitate the precipitation of further quantities of the salt.

The sols of United States patent No. 2,285,477 which contain from 0.5% to 25%, by weight of the sol, of a water-miscible organic liquid may be suitably modified to provide acidic silica hydro-organosols suitable for preparing the starting silica aerogels of the present invention by adding additional quantities of water-miscible organic liquid in amounts such that the sol contains from about 8 mols to about 20 mols of water-miscible organic liquid per mol of SiO₂. Stated differently the water-miscible organic liquid may be added to the sols until such sols contain at least 65% by weight, based on the weight of the sol, of water-miscible organic liquid. These sols normally have a relatively low salt content of about 0.1% to 2.0% by weight depending upon the amount of organic liquid used prior to cooling.

The starting acidic silica hydro-organosols employed in the processes of the present invention usually have a pH between 1.9 and 4.5 preferably between 2.7 and 3.5 and contain silica, water, 0.3% or less of the above-mentioned salt or electrolyte, and from 8 to 20 mols, preferably 10 to 14 mols per mol of SiO₂, of a substantially neutral,

water-miscible, organic liquid, preferably an organic liquid having a boiling point below that of water. The water and such organic liquid constitute a homogeneous liquid phase of the hydro-organosols.

The relationship of the amount of silica as SiO_2 and the amount of water-miscible organic liquid in the starting acidic hydro-organosols is important and the organo-silica aerogels of this invention will not usually be formed if the water-miscible organic liquid in the hydro-organosol is present in an amount substantially less than 8 mols per mol of SiO_2 . Although in some instances the silica hydro-organosols may contain more than 20 mols of the organic liquid per mol of SiO_2 , there is generally no advantage in such sols, and such sols tend to be expensive.

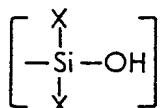
The silica content of the hydro-organosols employed in the processes of the present invention may vary considerably, but is usually between 1% and 9% by weight of the sol and is preferably in the range of from 3% to 7.5% by weight of the sol.

The neutral or substantially neutral water-miscible organic liquids which may be employed in the hydro-organosol used in the processes of this invention may have a boiling point below or above the boiling point of water. However, it is desirable and preferable to employ neutral, water-miscible organic liquids, more preferably those consisting of carbon, hydrogen and oxygen atoms, which have a boiling point below that of water at atmospheric pressure. As examples of the last-mentioned liquids may be mentioned monohydric alcohols such as methanol, ethanol, isopropanol, tertiary butyl alcohol; ketones such as acetone and methyl ethyl ketone and the like and aliphatic esters. The preferred organic liquids which are most suitably reactive with siloxy groups are the above-mentioned monohydric alcohols, and of these ethanol is particularly preferred.

In a preferred embodiment of this invention, the starting acidic silica hydro-organosols are preferably prepared from acidic silica aquasols which in turn are prepared by first reacting an aqueous solution of sodium silicate and aqueous sulfuric acid at a temperature of between about 0°C to 15°C in such proportions and concentrations as to provide an acidic silica aquasol having a pH of 1.8 to 4.5 and containing sodium sulfate and from 10% to 18% by weight of SiO_2 as silicic acid.

The silica aquasol thus formed is maintained at a temperature in the range of about 0°C to 15°C and a substantially neutral, water-miscible organic liquid, preferably ethanol, is mixed therewith to form a silica hydro-organosol containing from 65% to 85% of the organic liquid and from 3% to 7.5% by weight of SiO_2 as silicic acid and having a pH in the range of from 1.8 to 4.5. The amount of the organic liquid in the sol thus formed is from about 10 to about 14 mols per mol of SiO_2 in the sol. The sodium sulfate is substantially insoluble in the above sol and is almost entirely precipitated therefrom. On the removal of the Na_2SO_4 by centrifugation, filtration, or the like, a sol is obtained which contains from about 0.1% to 0.3% by weight of Na_2SO_4 depending upon the concentration of the organic liquid in the sol and the temperature of the sol.

The acidic silica hydro-organosols which are employed in the processes of the present invention are believed to contain aggregates of colloidal silica and/or polysilicic acid dispersed in the liquid phase thereof. It is believed that these aggregates initially range in size from 10 to 100 angstroms, as the sols are freshly prepared, but such aggregates continue to grow through siloxane polymerization as the sol ages and/or is heated until a hydro-organogel is formed. The rate at which such aggregates will grow generally depends on the concentration of the silica, temperature and the amounts of water-miscible organic liquid present in the sol as initially prepared. These silica sols containing the aggregates are further characterized in that the aggregates have a large number, e.g., 1,000 or more of silanol

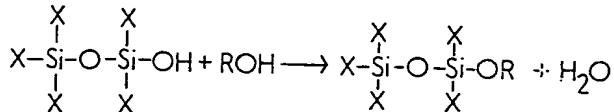


groups on their surfaces, where X in the accompanying formula may be either a siloxane radical, a polysiloxane radical as hereinbefore described, or a hydroxyl group. These aggregates are hydrophilic, yet water-insoluble, and are referred to herein as hydrophilic silica aggregates containing a multitude of silanol groups.

When such hydro-organosols, which comprise colloidally dispersed aggregates of hydrophilic silica or polysilicic acid containing a multitude of silanol groups and a relatively high concentration (e.g., from about 8 to 20 mols per mol of SiO_2) of water-

5 miscible organic liquid, are converted to a silica aerogel and are heated, a reaction takes place between some of the molecules of the organic liquid remaining in the aerogel and the siloxy or silanol groups. Although the exact nature of the reaction is unknown, the reaction in part is believed to be a condensation reaction in which, for example, an alcohol reacts with a silanol group substantially as follows:

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wherein R is an organic group or radical such as CH_3 , C_2H_5 , or the like and X is as previously described herein.

10 Such chemical bonding is believed to be accomplished as heat polymerization proceeds until some of the carbon atoms in the organic groups are chemically bound as hereinbefore indicated to a portion of the siloxy groups in the aerogel. The hydrogen atoms are believed to be bound in the polymer in the form of silanol groups and as hydrocarbon hydrogen.

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15 The starting silica aerogels employed in the processes of this invention may be prepared by heating the starting acidic silica hydro-organosols to form a silica hydro-organo gel, usually by charging the sol to a pressure-resistant vessel and converting the sol to a gel in situ. The silica hydro-organogels so formed, which contain polymerized siloxy groups are believed to contain some carbon and hydrogen atoms chemically bound to a portion of the siloxy groups as above described. These hydro-organogels 20 may then be converted to an aerogel by converting substantially all of the liquid phase to a vapor phase and separating the vapor phase without subjecting it to a substantial compressive liquid-solid interface, for example, in accordance with the liquid removal process of United States patent No. 2,093,454.

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25 In carrying out the removal of the liquid phase from the gel formed from the hydro-organosol it is necessary to heat the gel in a closed zone or system in which the pressure may be controlled as desired, for example, in an autoclave, at a temperature such that the liquid phase of the gel has been converted to a vapor, and thereafter the vapor may be released slowly from the closed system without appreciable shrinkage of the gel. This temperature may vary from about 30°C below the critical 30 temperature to about the critical temperature of the liquid phase of the gel, depending upon the particular organic liquid and concentration thereof, present in the liquid phase of the gel. The temperature is then maintained or raised, as desired, while releasing the vapor slowly until essentially all of the vapor is released from the closed 35 system. Although the temperature may be as much as 30°C below the critical temperature of the liquid phase of the gel in some instances, satisfactory results may be obtained at such a temperature. On the other hand, some shrinkage of the gel does occur, and it is preferred to avoid this shrinkage by operating at least at the critical temperature of the liquid phase of the gel. Higher temperatures may also be used, for example, temperatures up to about 500°C , but it is preferred not to exceed a temperature of about 350°C .

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40 As noted hereinbefore the silica aerogels so prepared may be converted to the novel organo-silica aerogels of this invention by heating, at atmospheric or elevated pressures, the silica aerogels at temperatures and for a time sufficient to form an organo-silica aerogel having a chemical composition and physical properties as hereinbefore described.

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45 In a preferred embodiment of one process of this invention the finely divided Group I organo-silica aerogels are advantageously prepared by simultaneously heating and comminuting the starting silica aerogels in an atmosphere of superheated steam at a pressure in the range of from 100 psig to 200 psig and at a temperature in the 50 range of from 150°C to 375°C until a finely divided Group I organo-silica aerogel is formed. The time required may vary to some extent, depending upon the temperature employed, but will usually vary from 3 seconds to 3 minutes, with the lower temperatures corresponding to the longer heating times.

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55 The heating and comminuting of the aerogels may be suitably accomplished by simultaneously introducing coarse particles (e.g. particles having a size such that they will pass through a No. 4 or No. 8 U.S. standard screen) of the starting silica-aerogels and pressurized, superheated steam into an enclosed chamber thereby utilizing the heat and mechanical energy and pressure of the steam to contact and to simultaneously heat and comminute or grind the aerogels.

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By so proceeding it is possible to obtain finely divided Group I organo-silica aerogels having an average particle size in the range of from about 1.0 to about 2.5 microns and a particle size distribution as hereinbefore described.

5 In a particularly advantageous embodiment of the process of this invention for producing the Group I organo-silica aerogels the starting silica aerogels are pre-ground to coarse particles having a particle size of 4 to 8 mesh, and are continuously introduced into a commercially available "steam grinding" mill such as for example a commercial "Jet-O-Mizer" mill manufactured by the Fluid Energy Processing Equipment Company of Philadelphia, Pennsylvania. The particles are introduced in the mill so as to be suspended in and contacted with pressurized superheated steam at a pressure of 10 from 140 psig to 200 psig and at a temperature of 250°C to 375°C for 3 to 30 seconds. The ground finely divided particles having the particle size range and distribution hereinbefore described are then continuously removed through a discharge opening in the mill.

15 The Group II organo-silica aerogels of this invention may be advantageously prepared by a process which comprises heating a starting silica aerogel, e.g. a starting silica aerogel prepared as hereinbefore described or a Group I organo-silica aerogel, preferably in an atmosphere of air and at atmospheric pressure and at a temperature in the range of from 350°C to 750°, preferably 600°C to 700°C until an organo-silica aerogel having the chemical composition and properties corresponding to the previously described Group II organo-silica aerogels, is formed. The heating times employed may vary widely depending upon the temperature used, but are usually within the range of from 15 seconds to 2 hours, preferably 30 to 90 seconds. Generally speaking, the shorter heating times correspond to the higher temperatures employed. In a preferred embodiment the Group II organo-silica aerogels are prepared by heating the Group I organo-silica aerogels at the preferred temperatures and times as above described. Although the organo-silica aerogels may be heated in a variety of ways commonly employed by those skilled in the art such as for example, in an oven or a kiln, it has been found particularly advantageous to heat the organo-silica aerogels in a finely divided and in a fluidized state, under the previously stated preferred conditions.

20 The range of heating temperatures employed (350°C to 750°C) is at or above the temperature range at which silanol groups are condensed to form siloxane or siloxy groups. It would normally be expected that all of the hydrogen from the silanol groups would be removed by condensation of the finely divided organo-silica aerogels from silanol to siloxane groups during the heating process. Also it would be expected that all of the organic carbon and hydrogen would be removed from the organo-silica aerogels at these temperatures. However, substantial amounts of the carbon and hydrogen atoms unexpectedly remain in the aerogel in a chemically combined state.

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In a particularly preferred embodiment of this invention relating to the preparation of Group II aerogels a finely divided, Group I organo-silica aerogel is introduced, together with air which has been heated to any temperature within the range of from 325°C to 700°C, preferably from 600°C to 700°C, into an elongated zone, such as a cylindrical chamber, through an opening at one end thereof. The heated air fluidizes and moves the finely divided silica aerogel through the length of the zone or chamber to a discharge opening. The residence time in the chamber is usually controlled by regulating the velocity of the heated air. Generally speaking, the velocity of the heated air employed will depend upon the temperature of the air. Thus, when the temperature of the air is at 700°C the velocity thereof may be so controlled that the dwell or residence time in the zone or chamber is only from 15 to 45 seconds. At lower air temperatures the velocity of the air may be controlled so that the dwell or residence time in the zone or chamber will be of the order of magnitude of from 30 to 90 seconds.

The two groups of finely divided organo-silica aerogels of this invention have substantially the same physical characteristics, that is, average particle size, specific surface area, external surface area, average pore diameter and total pore volume. The two groups of organo-silica aerogels differ, however, in the amounts of carbon and hydrogen atoms which are chemically bound to a portion of the siloxy groups as hereinbefore described and also differ in their thickening ability with respect to certain organic liquids as will be evident from the specific examples.

The novel organo-silica aerogels of the present invention are generally suitable for all applications and uses of previously described silica aerogels *per se* and additionally can be used as thickening agents in liquids in which the previously described silica aerogels cannot ordinarily be used in a satisfactory manner.

The desirability of thickening organic liquids for use in certain applications has been widely recognised and it has been proposed heretofore to thicken a variety of such liquids by incorporating therein inert inorganic materials including mica, diatomaceous earth, talc, alumina, graphite and the like, and in particular, silica aerogels. For example, it has been proposed, in United States patent No. 2,260,625 to thicken oily liquids, such as lubricating oils, and to convert such oils into greases by incorporating silica aerogels in amounts up to as high as 50% by weight of such oils. Silica aerogels described in United States patent Nos. 2,285,449 and 2,285,477 have also been used to thicken oils. Also, for example, it has been proposed in United States patent No. 2,892,730 to thicken organic liquids containing high molecular weight film formers, such as nitro-cellulose, cellulose acetate, polyvinyl acetate, chlorinated rubber and the like dissolved in organic solvents, with oxides of silicon, aluminum and titanium, to prevent the settling of mineral fillers therefrom.

It has also been proposed in United States patent No. 2,610,960, to thicken, and/or render thixotropic, coating and filling compositions such as polymerizable organic liquids consisting of liquid polyester resins by the incorporation of vermiculite in an amount as high as 50% by weight of the vermiculite in such liquids. It has also been proposed in United States patent No. 2,887,461 to render thixotropic, laminating compositions consisting of solid polyester resins dissolved in styrene by the incorporation of silica aerogels, such as the silica aerogels described in the aforesaid patents or mixtures of such a silica aerogel and alumina in amounts as high as 20% by weight of such inorganic materials in the liquids. By thickening and/or rendering such liquids thixotropic, it has been possible to overcome the problem of drainage of such compositions away from the coated or filled objects to which the composition has been applied.

However, the above-described thickening agents possess certain disadvantages, in that relatively large amounts of such materials are required to significantly thicken or increase the viscosity of organic liquids and/or render these liquids capable of forming thixotropic gels. Thus, for example, the thickening agents when used in large quantities, in some instances, adversely affect the properties of such organic liquids or the use thereof, while, in other instances, the cost of these thickening agents renders their use, in the large quantities normally required, economically prohibitive. Although silica aerogels of the type described in the aforementioned United States patents Nos. 2,285,449 and 2,285,477 have been used as thickening agents for oils, the utility of these materials is limited, particularly where it is desired to thicken polymerizable organic liquids, such as plastisols, polyesters and epoxide resins, prior to the curing of these materials. In using these liquid resins, the polymerizable resins, particularly polyesters, or solutions thereof are applied as filling and coating compositions or films as desired, following which the curing of the resin is caused to take place. One of the problems encountered in applying liquid resins, for example, in the fabrication of laminates such as fibre glass, is the tendency of the liquid to flow or drain away from the surface to which it is applied when such surface is not disposed in the horizontal plane as is frequently the case. Thus, it has been necessary to incorporate relatively large amounts, e.g. up to 20% by weight, of the silica aerogels of the patents just referred to in such polymerizable liquids to obtain thickening and prevent drainage, although it is known that amounts in excess of 5% by weight of silica aerogels in such liquids usually adversely affect the properties of the polymers when cured. Generally stated, the silica aerogels of the type described in the aforementioned patents are relatively inefficient and uneconomical for use as thickening agents for organic liquids.

According to a further feature of the present invention there are provided compositions which comprise an organic liquid and an amount, sufficient to thicken or increase the viscosity of such liquid, of an organo-silica aerogel as hereinbefore defined.

The amount of the novel, organo-silica aerogels which may be employed in the compositions of the present invention may vary to some extent, depending upon the particular organo-silica aerogel and organic liquid employed, the end use of the particular composition and the degree of thickening required. Generally speaking, compositions containing from 0.2% to 5.0% by weight of such novel aerogels, based on the weight of the composition, will effectively thicken or substantially increase the viscosity of organic liquids. As noted hereinbefore when prior art thickening agents including previously known silica aerogels are employed in thickening organic liquids such thickening agents are generally employed in amounts of from more than 6.0% up to 50% by weight of the composition.

Any of a wide variety of organic liquids may be employed in the compositions of this invention, but it has been found preferable to employ organic liquids which are liquid in the range of from -10°C to 100°C, more desirably in the range of from

0°C to 70°C, at atmospheric pressure. Also it has been found desirable to employ organic liquids having a viscosity in the range of from 2.5 millipoises to 3,000 centipoises at a temperature of about 25°C.

Thus, classes of organic liquids having a relatively low viscosity, e.g. in the range of from 2.5 to 25 millipoises at 25°C can be employed in combination with the novel organo-silica aerogels to provide compositions having a viscosity appreciably above 25 millipoises and up to 500 centipoises at this temperature. Such organic liquids may be organic solvents, for example, solvents used in paint, varnish or lacquer removers, and include liquids such as aliphatic and aromatic alcohols, ketones and esters, for example, ethanol, acetone, methyl ethyl ketone, ethyl acetate, amyl acetate and the like.

Also, classes of organic liquids having relatively higher viscosities, e.g. viscosities ranging from 100 to 600 centipoises at 25°C, can be used in combination with the novel organo-silica aerogels to provide compositions having viscosities of from 1,000 to 8,000 centipoises at 25°C. Such organic liquids include classes of oleaginous liquids such as oils of animal and vegetable origin, for example cod liver oil, olive oil, corn oil and the like. Also included are lubricating oils such as hydrocarbon motor oils and these may be employed in conjunction with the novel aerogels to provide gel-like bodies having a grease consistency.

In one embodiment of this invention, thin hydrocarbon lubricating oils such as motor oils having viscosities of between 90 and 110 centipoises may be thickened by the dispersion of from 0.2% to 1.5% of either the Group I or Group II organo-silica aerogels to provide compositions having viscosities of from 250 to 500 centipoises at 27°C when the viscosity measurements are taken on a MacMichael Viscosimeter with a No. 26 wire. More specifically a composition containing a light motor oil (SAE No. 10) and 0.5% by weight of a Group II organo-silica aerogel usually has a viscosity of from 300 to 350 centipoises at 27°C.

Other classes of organic liquids which may be thickened and/or rendered thixotropic include film-forming organic liquids such as liquids containing a dissolved organic film-forming or bonding solid or liquid which, on evaporation of such liquid or by polymerization during or after evaporation of such organic liquid, forms films, coatings or a binder which is capable of bonding two similar (e.g. glass fibres) or two dissimilar materials with a relatively high strength bond.

A particularly useful embodiment of the present invention comprises organic thixotropic compositions comprising natural and/or synthetic polymers in a liquid medium and containing relatively small amounts of the aforescribed finely divided, amorphous, Group I organo-silica aerogels.

The term "thixotropic" is used herein to denote the property of certain organic liquids, containing the novel organo-silica aerogels, to thicken and to change rapidly, on standing, from a liquid into a gel-like solid mass or body having sufficient cohesive strength to withstand distortion by gravitational force when suspended in an inverted receptacle or on a coated object. The gel is also of such a nature that it can be fluidized by the application of mechanical agitation as by shaking, stirring, vibrating and the like. The property of thixotropy as understood herein is thus characterized by a reversible isothermal sol-gel transition.

It has presently been found possible to thicken or to render a wide variety of organic liquid resin compositions thixotropic, by incorporating therein from 0.2% to 5.0% by weight, based on the weight of the liquid resin composition, of any of the herein-described novel, amorphous, organo-silica aerogels having a particle size in the range from 1.0 to 2.5 microns. For example, liquid coating compositions comprising solutions of high molecular weight film-formers dissolved in organic solvents may be thickened by dispersing in the solution from about 0.2% to about 1.0% by weight, based on the weight of the solution, of the organo-silica aerogels. Also certain organic liquid polymers may be made thixotropic by dispersing therein from 0.5% to 3.0% by weight, based on the weight of the composition of any of the organo-silica aerogels. Such compositions are generally employed as adhesives, films, foils, lacquers, paints, stretching lacquers (dopes) and the like and comprise solutions or suspensions of high molecular weight organic film-formers such as, for example, nitrocellulose, cellulose acetate, chlorinated rubber, polyvinyl acetate, polyvinyl chloride, polyacrylic esters, cellulose butyrate, cellulose propionate, and the like, which are dissolved or suspended as fine particles in organic solvents or liquids such as, for example, acetone, ethanol, ethyl acetate, amyl acetate or dioctyl phthalate.

These compositions usually contain from about 40% to 50% by weight of film-formers dissolved or suspended in an organic solvent or liquid and may often have a

dispersed phase consisting of pigments or fillers which settle out after standing for relatively short periods of time. Such settling is generally prevented by adding a small amount, e.g. from about 0.2% to 0.5% of the novel organo-silica aerogels to these compositions. Where it is desired that the above described liquid compositions be applied to objects in the form of a spray or spreadable liquid, the addition of from 0.5% to 3% by weight (depending upon the amount of film-forming materials in the composition) of any of the novel organo-silica aerogels to such compositions will cause them to form thixotropic gels almost immediately on contact with the object to which they are applied and the compositions will then not run or drain from such objects.

Among the compositions referred to above which may be employed with the novel organo-silica aerogels to form a particularly useful embodiment of this invention are plastisol compositions comprising halogenated vinyl or vinylidene resins such as, for example, an emulsion polymerized polyvinyl chloride polymer suspended in a plasticizer such as a phthalate ester, for example, dioctyl phthalate, dibutyl phthalate, dihexyl phthalate, ethyl hexyl phthalate and the like, in which the plasticizer chosen is a plasticizer for the resin employed. Such plastisol compositions are exemplified in United States patent Nos. 2,852,482 and 2,885,378. Since plastisol compositions are used in molding films they must be liquid or at least have an element of fluidity. However, when in the liquid state the halogenated vinyl or vinylidene resin particles and fillers or pigments, which fillers or pigments are often incorporated in such compositions, tend to settle out and render the plastisol composition non-homogeneous and unsuitable for molding films. It has been found that the addition of from 0.2% to 5.0% preferably from 0.2% to 3.0% by weight of the organo-silica aerogels to such compositions will thicken the composition to the point where it will remain fluid or will form a thixotropic gel which can be transformed to a fluid state by mechanical agitation thereby preventing settling or separation of components within the plastisol compositions.

It has also been found possible to thicken and/or render thixotropic, polymerizable organic liquid compositions comprising polymerizable resins including solventless varnishes and polyester resin compositions which are used in coating, filling, adhesive and laminating operations by incorporating small amounts of the organo-silica aerogels therein. Such compositions include liquid alkyd resins or solutions of solid alkyd or polyester resins dispersed in a solvent, (for example, styrene) which is usually copolymerizable with the polyester resin.

Other liquids which may be employed in combination with the novel organo-silica aerogels in a preferred embodiment of this invention are polymerizable liquids comprising unsaturated alkyd resins. These resins are the reaction products of polyhydric alcohols, mixtures of polyhydric alcohols or mixtures of polyhydric and monohydric alcohols, and an alpha-unsaturated, alpha, beta-carboxylic acid, or a plurality of polycarboxylic acids one of which at least is an unsaturated polycarboxylic acid. Examples of such polyhydric alcohols are ethylene glycol, di- and triethylene glycol, propylene glycol, tetramethylene glycol, glycerine or pentaerythritol in combination with a monohydric alcohol. Examples of unsaturated polycarboxylic acids are maleic, fumaric and itaconic acids. The term polycarboxylic acid as used herein is intended to include within its meaning the anhydrides of such acids which may also be employed. In addition to one or more of the unsaturated polycarboxylic acids, saturated polycarboxylic acids may also be present in the reaction mixture referred to above. Examples of such saturated polycarboxylic acids are succinic, adipic, sebacic and phthalic acids. The anhydrides of such acids may also be used.

In addition to the above unsaturated alkyd resins, the polymerizable liquids which may be used in the compositions of the present invention may contain polymerizable substances such as, for example, esters of monohydric alcohols and polycarboxylic acids, including unsaturated polycarboxylic acids, halogenated aromatic polycarboxylic acids and polybasic inorganic acids. Examples of such substances are dialkyl maleate, dialkyl fumarate, dialkyl itaconate, dialkyl chlorophthalates, trialkyl phosphate and the like. Other substances which may be incorporated in these polymerizable liquids are esters of monohydric alcohols and unsaturated polycarboxylic acids which are capable of copolymerizing with unsaturated alkyd resins such as, for example, dioctyl itaconate, dibenzyl itaconate, diethyl fumarate, dibenzyl fumarate and the like.

Esters of acrylic and methacrylic acids may also be used in the present compositions. Examples of such esters are methyl, ethyl, propyl, isopropyl, butyl and isobutyl acrylates and the corresponding esters of methacrylic acid. Vinyl monomers may also be used in such compositions including styrene, vinyl acetate, vinyl chloride and combinations thereof and the like.

The above described unsaturated resins may be liquids or solids dissolved in organic liquids and the finely divided amorphous organo-silica aerogels may be directly dispersed in the liquids. When the unsaturated resin is a solid, it is necessary to dissolve the resin in an organic solvent, preferably a solvent which is copolymerizable with the polyester resin, such as, for example, styrene.

There may also be incorporated in the above described polymerizable liquid compositions, small amounts ranging from about 0.5% to 2.0% by weight, based on the weight of the polymerizable liquid, of a polymerization catalyst. Many types of polymerization catalysts, well known to those skilled in the art, may be incorporated in the polymerizable liquid compositions of this invention including, for example, benzoyl peroxide, methyl ethyl ketone, peroxide, cyclo-hexane peroxide and cumene hydroperoxide, which provide the oxygen necessary to effect polymerization.

Generally speaking, when a solid polyester resin is dissolved in an organic solvent the resulting liquid will contain from 30% to 80% by weight of the polyester resin. In one embodiment of this invention it has been found possible to prepare a thixotropic gel composition when a solution of an unsaturated polyester resin of a polyhydroxy alcohol and an unsaturated polycarboxylic acid was dissolved in 40%, based on the weight of the polyester, of styrene and from 1% to 2.5% of either of the novel organo-silica aerogels was dispersed therein. When 1.0% by weight of such organo-silica aerogel is dispersed in the aforementioned resin solution the viscosity of such solution is usually increased from about 850 centipoises to about 3,400 poises at 25°C where the viscosity measurements are made with a standard Brookfield Model RVT Synchroelectric Viscosimeter operated at a speed of 20 rpm. The composition on standing for from 9 to 15 seconds usually becomes a solid mass which reverts to a liquid upon being stirred. On the other hand, a 1% dispersion of a silica aerogel such as described in the United States patents Nos. 2,285,449 and 2,285,477, when added to the above resin composition, results in a viscosity of only 1,160 centipoises when measured as above described and remains in a liquid state upon standing for more than 8 hours.

The following examples will serve to illustrate the invention; parts and percentages are by weight unless otherwise specified.

EXAMPLE I

Twenty-one hundred parts of an acidic silica ethanol-aquasol having a pH of 2.9 and containing 11% SiO₂, 50% ethanol, 0.3% Na₂SO₄, and the remainder consisting of water was diluted with 950 parts of 2B ethanol to form an ethanol-aquasol having 10 mols of ethanol per mol of SiO₂ and containing 7.3% SiO₂, 65.6% ethanol, less than 0.2% Na₂SO₄, and the balance water. (2B ethanol is denatured alcohol containing 0.5 gallon of benzene per 100 gallons of 190 proof ethyl alcohol). The diluted sol had a pH of 3.4 and contained about 11 mols of ethanol per mol of SiO₂. The bulk of the ethanol-aquasol was charged to an autoclave until 75% of the volume of the autoclave was occupied by the sol. The autoclave was then closed and heated until a pressure of 1900 psig (which was slightly above the critical pressure) was attained. Heating was continued and the ethanol-water vapor was released intermittently from the autoclave to maintain the pressure of 1900 psig until a temperature of 300°C was obtained. This temperature was above the critical temperature of the liquid phase of the ethanol aquagel. The vapor in the autoclave was released slowly until substantially all of the vapor was removed and the autoclave was then cooled. A light aerogel having a density of 3 pounds per cubic foot and the bulk of which consisted of 95% air was obtained.

The silica aerogel was then ground in an air attrition mill at an air pressure of 58 pounds per square inch gauge at a temperature of 200°C for 10 seconds to provide a finely divided amorphous material (a Group I organo-silica aerogel) having an average particle size of 2.4 microns and an external surface area of 1.88 square meters per gram, both measurements being determined by the method of J. H. L. Watson in Volume 20, page 576 of Analytical Chemistry (1948) and a total surface area of 275 square meters per gram as measured (using nitrogen gas) by the Method of Brunauer, Emmet and Teller described in "Advances in Colloid Science," Volume I, pages 1—36 (1942) published by Interscience Publishers, Incorporated, New York, New York.

The above material was analyzed for carbon and hydrogen and was found to contain 1.19% carbon and 1.39% hydrogen. The material had an SiO₂:C ratio of 15:1 and a SiO₂:H ratio of 1.1:1. When 1.6% by weight of this organo-silica aerogel was dispersed in a plastisol, specifically a liquid commercial plastisol containing polyvinyl chloride and dioctyl phthalate, the viscosity (Brookfield) increased from 4,000 centipoises to 132,000 centipoises at 25°C. The viscosity measurements were made with a

standard Brookfield Model HAT Synchro-electric Viscosimeter at 5 rpm viscosimeter speed.

On the other hand a finely divided silica aerogel was prepared from an acidic silica ethanol aquasol having a SiO₂ content of 11% by weight and containing 50% by weight of alcohol, 0.02% by weight of Na₂SO₄ and the balance consisting of water and having a pH of 3.0. The silica aerogel so prepared contained traces (e.g. 0.05% by weight) of carbon, 0.056% by weight of hydrogen and had an SiO₂:C ratio of 350:1 and an SiO₂:H ratio of 3:1. The aerogel was further characterized in having an average particle size of 2.6 microns, a specific surface area 332 square meters per gram, an external surface area of 0.77 square meters per gram and a total pore volume of 730 milliliters per gram.

When the silica aerogel so prepared was added to the above described uncured liquid polyester resin, almost 5.0% by weight of the aerogel was required to thicken the polyester resin to a viscosity of 132,000 centipoises at 25°C. Moreover, when the silica aerogel described in the preceding paragraph was heated within the range of 600 to 700°C in an atmosphere of air, such heating did not substantially increase the thickening capacity of the silica aerogel.

EXAMPLE II

A portion of the organo-silica aerogel prepared as described in the first two paragraphs of Example I was placed in trays and heated in an electric oven in air and at atmospheric pressure at 350°C for 2 hours. The material (a Group II organo-silica aerogel) so obtained contained 0.6% of carbon and 1.05% hydrogen and had substantially the same physical characteristics, that is, particle size and specific surface area as the organo-silica aerogel of Example I. This material had an SiO₂:C ratio of 25:1 and an SiO₂:H ratio of 1.4:1.

The heated finely divided organo-silica aerogel (2% by weight) was dispersed in a liquid uncured commercial polyester resin "Marco 28C" (produced by Celanese Corporation of America) comprising a condensation product of a polyhydroxy alcohol and an unsaturated polycarboxylic acid dissolved in styrene. The viscosity at 20 rpm (Brookfield) was increased from 850 centipoises to 3600 centipoises at 25°C. On the other hand, a 6% dispersion of a finely divided silica aerogel described in the next to last paragraph of Example I in the same polyester resin resulted in a viscosity (Brookfield) of only 2500 centipoises.

Group I organo-silica aerogels were prepared, using the processes described in the first two paragraphs of Example I and Group II organo-silica aerogels were prepared using the processes described in the initial paragraph of Example II, except that the starting hydro-organo sols contained methanol, isopropanol and acetone respectively, instead of ethanol. In each instance, the Group I organo-silica aerogels produced by the procedures of Example I contained from 1.0% to 1.3% of carbon and from 1.2% to 1.5% of hydrogen and had an SiO₂:C ratio of between 10:1 and 25:1 and an SiO₂:H ratio of 0.77:1 to 1.3:1. After these organo-silica aerogels were processed using the procedures described in Example II, they contained from 0.4% to 0.6% by weight of carbon and from 1.1% to 1.4% of hydrogen. The organo-silica aerogels so prepared efficiently thickened liquid polyvinyl chloride plastisol and polyester resin compositions, but the Group I organo-silica aerogels more efficiently thickened plastisols and the Group II organo-silica aerogels more efficiently thickened liquid uncured polyester resins.

EXAMPLE III

A silica aerogel, prepared according to the procedures described in the first two paragraphs of Example I was heated at 200°C in air at a pressure of 75 psig in a pressure chamber for 10 seconds and was thereafter ground in a laboratory ball mill. The product so obtained was a finely divided powdered organo-silica aerogel and when analyzed, was found to have substantially the same chemical composition and physical and thixotropic properties as the organo-silica aerogel described in Example I.

EXAMPLE IV

A silica aerogel prepared according to the method described in the first two paragraphs of Example I was heated in air at 200°C at a pressure of 75 psig for 10 seconds and was thereafter heated in air at atmospheric pressure in a laboratory furnace at a temperature of 400°C for one hour and forty-five minutes. The organo-silica aerogel so produced was then ground in a ball mill to a finely divided powder which, when analyzed, was found to have substantially the same chemical composition as the

organo-silica aerogel described in Example II. When tested for its ability to thicken polyester resins using the procedure described in Example II, the finely divided organo-silica aerogel was found to have substantially the same thickening capacity as the organo-silica aerogel described in Example II.

5 EXAMINE V

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Twenty-one hundred parts of an acidic silica ethanol aquasol having a pH of 2.9 and containing 11% SiO₂, 50% ethanol and 0.3% Na₂SO₄ and the remainder consisting of water was diluted with 950 parts of 2B ethanol to form an ethanol-aquasol having an ethanol:SiO₂ mol ratio of 10:1 and containing 7.3% SiO₂, 65.6% ethanol, less than 0.2% Na₂SO₄ and the balance water. The diluted sol had a pH of 3.4.

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The bulk of the diluted ethanol-aquasol was charged to an autoclave until 75% of the volume of the autoclave was occupied by the sol. The sol was then heated in the autoclave at 50°C until an ethanol-aquagel was formed. The autoclave was then closed and heated until a pressure of 1900 psig (which was slightly above the critical pressure) was attained. Heating was continued and the ethanol-water vapor was released intermittently from the autoclave to maintain the pressure at 1900 psig until a temperature of 300°C was obtained. This temperature was above the critical temperature of the liquid phase of the ethanol-aquagel. The vapor in the autoclave was released slowly until substantially all of the vapor was removed and the autoclave cooled. A light aerogel having a density of 3 pounds per cubic foot and the bulk of which consisted of 95% air, was obtained.

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The silica aerogel was then mechanically ground in air at room temperature in a laboratory mill until the particles of the ground material had a particle size of between 4 and 8 mesh, that is, all of the particles passed through a No. 4 mesh U.S. standard screen, but were retained on a No. 8 mesh U.S. standard screen. The material was then ground in a steam grinding mill, specifically a Model 0405 "Jet-O-Mizer" mill manufactured by the Fluid Energy Mill and Processing Company of Philadelphia, Pennsylvania. The mill was equipped with an opening adjacent to internally placed steam jets. The silica aerogel was introduced into the mill and almost immediately contacted with superheated steam, at a temperature of 300 to 375°C, which was continually introduced through the nozzles. The particles were suspended and agitated in the superheated steam which rapidly built-up a pressure in the mill which varied between 140 psig and 200 psig. The force of the steam simultaneously ground and transported the particles to a discharge opening in the mill where they were discharged into a receptacle.

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The product obtained was a light (1 pound per cubic foot) white, finely divided Group I, organo-silica aerogel powder. Particle size determinations, conducted as previously described, showed that the particles had an average particle size of 2.0 microns. The particle size distribution determined by centrifugation techniques was such that 24% of the particles had a particle size of between 0.5 and 1.0 microns, 26% had a particle size of between 1 and 2 microns, 27% of the particles had a particle size of between 2 and 3 microns, 17.5% of the particles had a particle size of between 3 and 4 microns and 5.5% of the particles had a particle size greater than 4, but less than 6 microns.

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45 Based on specific surface area and external surface area determinations conducted as previously described, the product had a total surface area of 340 square meters per gram and an external surface area of 1.90 square meters per gram. Pore volume and pore diameter determinations showed the product had a total pore volume of 745 milliliters per gram and an average pore radius of 110 angstroms.

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50 A chemical analysis for carbon and hydrogen showed that the product was an organo-silica aerogel which contained 1.14% by weight of carbon and 1.37% by weight of hydrogen, demonstrating an SiO₂:C ratio of 15:1 and an SiO₂:H ratio of 1.3:1.

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55 When 1.6% by weight of this material was dispersed in a liquid commercial plastisol consisting of polyvinyl chloride and dioctyl phthalate the viscosity (Brookfield) increased from 4,000 centipoises to 133,000 centipoises at 25°C. On the other hand a 6.0% dispersion of a prior art silica aerogel, prepared as described in the next to the last paragraph of Example I, in such plastisol resulted in a viscosity (Brookfield) of only 130,000 centipoises at 25°C. The viscosity measurements were made using the apparatus described in the third paragraph of Example I.

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EXAMPLE VI

The finely divided organo-silica aerogel of Example V was fed to a commercial air circulating heater, the circulating air in the heater and the heater itself being maintained at a temperature of 650°C. (The heating unit employed is manufactured commercially by the General American Transportation Company and is known as a Fluidizer Heater.) The finely divided organo-silica aerogel particles were suspended in the heated air in this heater for 35 seconds and discharged therefrom into a suitable receptacle. The material obtained was a Group II organo-silica aerogel which contained 0.5% of carbon and 1.1% by weight of hydrogen, demonstrating an SiO₂:C ratio of 36:1 and an SiO₂:H ratio of 1.4:1.

The finely divided product was a light (1 pound per cubic foot density) Group II organo-silica aerogel powder and was examined for specific surface area, external surface area, particle size, particle size distribution, pore volume and pore diameter according to the methods previously described. Based on this examination the finely divided product had an average particle size of 2.0 microns. The particle size distribution was such that 26% of the particles had a particle size of between 0.5 and 1 micron, 25% of the particles had a particle size of between 1 and 2 microns, 27% of the particles had a particle size in the range of between 2 and 3 microns, 16.5% of the particles had a particle size of between 3 and 4 microns and 5.5% of the particles had a particle size greater than 4 but less than 6 microns.

The product also had a total surface area of 350 square meters per gram, an external surface area of 1.9 meters per gram, a total pore volume of 750 milliliters per gram and an average pore radius of 115 angstroms.

When 2% by weight of the finely divided organo-silica aerogel was dispersed in the liquid uncured commercial polyester resin described in Example II the viscosity (Brookfield) was increased from 850 centipoises to 3,750 centipoises at 25°C. On the other hand a 6% by weight dispersion of the prior art silica aerogel prepared as observed in the next to last paragraph of Example I in the same polyester resin resulted in an increase in viscosity (Brookfield) to only 2,560 centipoises at 25°C.

EXAMPLE VII

A finely divided amorphous organo-silica aerogel (hereinafter designated as the Group I silica aerogel) comprising a silica polymer having siloxy groups and containing 1.14% by weight of carbon and 1.37% by weight of hydrogen and having an SiO₂:C ratio of 15:1 and an SiO₂:H ratio of 1.3:1, and further having an average particle size of 2.0 microns, a total surface area of 340 meters per gram and an external surface area of 1.9 square meters per gram was mechanically dispersed by means of an electric stirrer in two light, motor oils in the amounts indicated in the table at the end of this example. Viscosity measurements (also included in the table) were used as an index of thickening.

A finely divided amorphous, organo-silica aerogel (hereinafter designated as the Group II organo-silica aerogel) comprising a silica polymer having siloxy groups and containing 0.5% by weight of carbon and 1.1% by weight of hydrogen and having an SiO₂:C ratio of 36:1 and an SiO₂:H ratio of 1.4:1 and having substantially the same particle size, total surface area and external surface area as the Group I organo-silica aerogel was mechanically dispersed by means of an electric stirrer in two light motor oils in the amounts indicated in the following table in which viscosity measurements were used as an index thickening.

Composition	Viscosity Brookfield (Centipoises at 27°C.)
SAE No. 10 Motor Oil	100
SAE No. 10 Motor Oil + 0.5% Group I organo-silica aerogel	300
SAE No. 10 Motor Oil + 0.5% Group II organo-silica aerogel	280
SAE No. 20 Motor Oil	130
SAE No. 20 Motor Oil + 0.3% Group I organo-silica aerogel	350
SAE No. 20 Motor Oil + 0.3% Group II organo-silica aerogel	310

The motor oils were substantially thickened by the dispersion therein of the organo-silica aerogels as indicated above. By contrast when the same amount of a finely divided, previously known silica aerogel containing 0.05% carbon and 0.056% by weight of hydrogen, e.g. a silica aerogel such as that described in United States Patents Nos. 5 2,285,449 and 2,285,477 was added to the above oils no appreciable thickening occurred.

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EXAMPLE VIII
10 The Group I and Group II organo-silica aerogels described in the first two paragraphs of Example VII were mechanically dispersed with an electric stirrer in the following lacquer compositions to provide the following film-forming resin compositions.

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Composition Number Ingredients	1 gms	2 gms	3 gms	4 gms	5 gms	6 gms
Polyvinyl Chloride	15.0	—	—	15.0	—	—
Nitrocellulose	—	13.0	—	—	13.0	—
Cellulose Acetate	—	—	7.5	—	—	7.5
Ethyl Acetate	85.0	31.0	23.0	85.0	31.0	23.0
Ethanol	—	36.0	26.0	—	36.0	26.0
Toluol	—	—	11.0	—	—	11.0
Titanium Dioxide	1.5	—	—	1.5	—	—
Castor Oil	0.3	1.2	1.1	0.3	1.2	1.1
*Group I Organosilica Aerogel	0.3	0.6	1.0	—	—	—
*Group II Organosilica Aerogel	—	—	—	0.3	0.6	1.0

Added and dispersed after initial viscosity measurement

The viscosity of the compositions were tested by measuring the seconds-bubble-rise at 25°C in a Gardner tube before and after the incorporation of the organo-silica aerogels and the results obtained were as follows:

Composition	Viscosity in Seconds	
	Initial	After Aerogel Dispersion
1	4	250
2	5	410
3	4	600
4	4	220
5	5	430
6	4	580

5 In contrast when the same amounts of a previously known silica aerogel such as
that described in the last paragraph of Example VII were added to the foregoing
compositions, the viscosity of the composition (e.g. seconds bubble rise) did not exceed
40 in any given instance.

5

10 The following plastisol compositions were prepared in which an emulsion-polymerized polyvinyl chloride polymer was suspended in dioctyl phthalate containing di-basic lead phosphite (which phosphite was employed as a stabilizer to prevent decomposition during the heating of the plastisol). To these liquid plastisol compositions the organo-silica aerogels described in Example VII were added in the amounts indicated
15 in the following table.

10

15

Composition Number Ingredients	7 gms	8 gms	9 gms	10 gms	11 gms	12 gms	13 gms
Polyvinyl Chloride	100	100	100	100	100	100	100
Dioctyl Phthalate	80	80	80	80	80	80	80
Dibasic Lead Phosphite	3	3	3	3	3	3	3
Group I Organosilica Aerogel	1	—	3	—	5	—	—
Group II Organosilica Aerogel	—	1	—	3	—	5	—

The viscosities were measured in a Model HAT Brookfield Viscosimeter using a No. 6 spindle at 2.5 rpm, the values obtained being shown in the following table.

Composition	Viscosity in Poises (25°C.)
7	140
8	190
9	2,000
10	1,500
11	15,000
12	10,000
13	50

When a silica aerogel per se such as that described in the last paragraph of Example VII or an aminated silicate clay, e.g. Bentone (Registered Trade Mark), were added to the above compositions in place of the organo-silica aerogels it was necessary to add about 20 grams of each material to the compositions in order to obtain compositions having a viscosity of 10,000 poises.

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EXAMPLE X

An unsaturated polyester resin was prepared by reacting 50 mol per cent of phthalic anhydride and 50 mol per cent of maleic anhydride with a 25% molar excess of propylene glycol which excess propylene glycol was then distilled off leaving a solid, hard, brittle, unsaturated polyester resin. A solution was prepared by dissolving 60 parts by weight of the above described polyester in 40 parts of styrene. The Group I and Group II silica aerogels described in Example VII were separately admixed with portions of the above polyester resin-styrene compositions in a ball mill for one hour in the amounts indicated below. The viscosities were measured using the Model RVT Brookfield Viscosimeter at 20 rpm and at a temperature of 25°C.

Composition Number Ingredients	14 %	15 %	16 %	17 %	18 %	19 %
Polyester -Styrene Solution	99.5	99.0	98.5	99.5	99.0	98.5
Group I Silica Aerogel	0.5	1.0	1.5	—	—	—
Group II Silica Aerogel	—	—	—	0.5	1.0	1.5

Compositions 15, 16, 18 and 19 when allowed to stand for 30 seconds or more developed into a gel-like solid having the consistency of a light grease. Upon mechanical agitation, as provided by the Brookfield Viscosimeter, these compositions were immediately transformed into liquids having the viscosities listed in the following table. Compositions 14 and 17 did not form gels upon standing.

20

Composition	Viscosity Brookfield (20 rpm) (Centipoises)
14	2,900
15	3,300
16	3,900
17	2,700
18	3,200
19	3,600
Polyester-Styrene Solution per se	800

When the above polyester-styrene solution was formulated into compositions wherein like amounts of the aerogel described in the last paragraph of Example VII were used in place of the organo-silica aerogels, the viscosity of such compositions did not exceed 900 centipoises in any instance nor did any composition form a thixotropic gel.

5

EXAMPLE XI

Liquid resin compositions were prepared by mixing the amounts of the following ingredients:

Composition Number Ingredients	20	21	22	23	24
	(Parts by weight)				
Glyceryl Tris Cyclohexyl Maleate	30.0	20.0	—	—	35.0
10 Dioctyl Phthalate	30.0	20.0	0.2	0.4	18.0
Tertiary Butyl Perbenzoate	0.6	0.4	—	—	0.6
Vinyl Acetate-Chloride Copolymer	—	20.0	—	—	20.0
Decarboxylated Castor Oil	—	—	14.0	24.0	—
Butyl Methacrylate Monomer	—	9	—	—	14.8

10	Glyceryl Tris Cyclohexyl Maleate	30.0	20.0	—	—	35.0	10
Dioctyl Phthalate	30.0	20.0	0.2	0.4	18.0		
Tertiary Butyl Perbenzoate	0.6	0.4	—	—	0.6		
Vinyl Acetate-Chloride Copolymer	—	20.0	—	—	20.0		
Decarboxylated Castor Oil	—	—	14.0	24.0	—		
Butyl Methacrylate Monomer	—	9	—	—	14.8		

The above compositions were highly fluid and drained readily from glass rods that were dip coated therewith. When 1.5% of the Group I and Group II organo-silica aerogels described in Example VII were stirred into separate portions of each of the above compositions the resulting mixtures became highly thixotropic and glass rods dip coated with these compositions exhibited no drainage. However, when 5.0% by weight of the silica aerogel described in the last paragraph of Example VII was stirred into the above compositions and glass rods were subsequently dip coated therewith, considerable drainage occurred in a manner similar to that of the original resin compositions.

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The $\text{SiO}_2:\text{C}$ and $\text{SiO}_2:\text{H}$ ratios herein set forth were calculated by converting the weight per cent of SiO_2 in the silica aerogel and the weight per cent of carbon and hydrogen on the silica aerogel to mol percentages. The $\text{SiO}_2:\text{C}$ ratios were calculated by dividing the mol per cent of carbon into the mol per cent of the SiO_2 . The $\text{SiO}_2:\text{H}$ ratios were calculated by dividing the mol per cent of hydrogen into the mol per cent of SiO_2 .

WHAT WE CLAIM IS:—

1. An amorphous organo-silica aerogel comprising a silica polymer having siloxy groups and containing carbon and hydrogen atoms chemically bound to a portion of the siloxy groups in said aerogel, said aerogel having an SiO₂ to carbon atom ratio of from 10:1 to 50:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 2:1.

2. An aerogel according to claim 1 having an SiO₂ to carbon ratio of 10:1 to 25:1 and a SiO₂ to hydrogen ratio of 0.77:1 to 1.3:1.

3. An aerogel according to claim 1 or 2 containing from 0.4% to 1.2% by weight of carbon and from 0.9% to 1.5% by weight of hydrogen chemically bound to a portion of the siloxy groups.

4. An aerogel according to any of claims 1—3 having a total surface area of from 100 to 400 square meters per gram, and an external surface area of from 1.75 to 1.95 square meters per gram.

5. A finely divided amorphous organo-silica aerogel comprising a silica polymer having siloxy groups and containing carbon and hydrogen atoms chemically bound to a portion of the siloxy groups in said aerogel, said aerogel being characterized in having a total surface area of from 100 to 400 square meters per gram and an external surface area of from 1.75 to 1.95 square meters per gram, an average particle size in the range of from 1.0 to 2.5 microns and containing from 0.9% to 1.2% by weight of carbon and from 1.2% to 1.5% by weight of hydrogen, said aerogel being further characterized in having an SiO₂ to carbon atom ratio of from 10:1 to 25:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 1.3:1.

6. An aerogel according to claim 5 having a total surface area of from 250 to 350 square meters per gram.

7. A finely divided amorphous organo-silica aerogel comprising a silica polymer having siloxy groups and containing carbon and hydrogen atoms chemically bound to a portion of the siloxy groups in said aerogel, said aerogel being characterized in having a specific surface area of from 250 to 350 square meters per gram, an external surface of from 1.75 to 1.95 square meters per gram, an average particle size in the range of from 1.0 to 2.5 microns, and containing from 0.4% to 0.8% by weight of carbon and from 0.9% to 1.2% by weight of hydrogen, said aerogel being further characterized in having an SiO₂ to carbon atom ratio of 25:1 to 50:1 and an SiO₂ to hydrogen atom ratio of 1.3:1 to 2.0:1.

8. An aerogel according to claim 1 substantially as hereinbefore described with reference to any of Examples I to VI hereinbefore set forth.

9. A process of preparing an organo-silica aerogel which comprises (1) heating an acidic silica hydro-organosol having a pH of from 1.8 to 4.5 and comprising (a) silica, (b) from 8 to 20 mols, per mol of SiO₂, in said sol, of a substantially neutral, water-miscible organic liquid and (c) water thereby forming a gel, (2) heating the gel in a closed system without subjecting it to a substantial compressive liquid-solid interface until substantially all of the liquid phase of the gel has been converted to a vapor phase, (3) separating said vapor from said gel thereby forming an aerogel and (4) heating said aerogel at a temperature and for a time sufficient to form an organo-silica aerogel comprising a silica polymer having siloxy groups and containing carbon and hydrogen atoms chemically bound to a portion of the siloxy groups in said organo-silica aerogel, said organo-silica aerogel being further characterized in having an SiO₂ to carbon atom ratio of from 10:1 to 50:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 2:1.

10. A process according to claim 9 wherein step (4) is effected by heating said aerogel at a pressure of from 10 psig to 200 psig at a temperature in the range of from 90°C to 750°C until an organo-silica aerogel is formed.

11. A process according to claim 9 wherein step (4) is effected by heating the aerogel at a pressure of from 10 psig to 200 psig at a temperature in the range of from 90°C to 375°C until an organo-silica aerogel is formed.

12. A process according to any of claims 9—11 wherein the organic liquid is methanol, ethanol or isopropanol.

13. A process according to claim 9 wherein step (4) is effected by heating said

aerogel at a temperature in the range of 350°C to 750°C until an organo-silica aerogel is formed.

5 14. A process according to claim 13 wherein step (4) is effected by heating said aerogel at a pressure of from 10 psig to 200 psig at a temperature in the range of from 90°C to 375°C until an organo-silica aerogel is formed and thereafter heating the product at a temperature in the range of from 350°C to 750°C for 15 seconds to 2 hours. 5

10 15. A process according to claim 13 or 14 wherein the water-miscible organic liquid is ethanol.

10 16. A process of preparing a finely divided organo-silica aerogel which comprises (1) heating an acidic silica hydro-organosol having a pH of from 1.8 to 4.5 and comprising (a) colloidal silica, (b) from 10 to 14 mols, per mol of SiO₂, in said sol, of ethanol and (c) water, thereby forming a gel, (2) heating the gel in a closed system without subjecting it to a substantial compressive liquid-solid interface until substantially all of the liquid phase of the gel has been converted to the vapor phase, (3) separating said vapor from said gel thereby forming an aerogel and (4) simultaneously heating and comminuting said aerogel in an atmosphere of superheated steam at a pressure of from 100 psig to 200 psig and at a temperature in the range of from 150°C to 375°C until a finely divided organo-silica aerogel is formed. 10

15 17. A process according to claim 16 wherein the finely divided organo-silica aerogel produced is subsequently heated at a temperature of from 350°C to 750°C for from 15 seconds to 2 hours. 15

20 18. A process of preparing a finely divided organo-silica aerogel which comprises (1) heating an acidic silica hydro-organosol having a pH in the range of from 2.7 to 3.5 and containing (a) from 3% to 7.5% by weight of silica, (b) at least 65% by weight of ethanol and (c) water, thereby forming a gel, (2) heating the gel in a closed system without subjecting it to a substantial compressive liquid-solid interface until substantially all of the liquid phase of the gel has been converted to the vapor phase, (3) separating said vapor from said gel thereby forming an aerogel and (4) simultaneously heating and comminuting said aerogel in an atmosphere of superheated steam at a pressure of from 100 psig to 200 psig and at a temperature in the range of from 150°C to 375°C until a finely divided organo-silica aerogel is formed. 20

25 19. A process according to claim 18 wherein the finely divided organo-silica aerogel produced is subsequently heated at a temperature in the range of 600°C to 700°C for from 30 seconds to 90 seconds. 25

30 20. A process of preparing a finely divided organo-silica aerogel which comprises (1) heating an acidic silica hydro-organo sol having a pH in the range of from 2.7 to 3.5 and containing (a) from 3% to 7.5% by weight of silica, (b) at least 65% by weight of ethanol and (c) water, thereby forming a gel, (2) heating the gel in a closed system without subjecting it to a substantial compressive liquid-solid interface until substantially all of the liquid phase of the gel has been converted to the vapor phase, (3) separating said vapor from said aerogel and (4) simultaneously heating and comminuting said aerogel in an atmosphere of superheated steam at a pressure of from 100 psig to 200 psig and at a temperature in the range of 250°C to 375°C for from 3 to 50 seconds to form a finely divided organo-silica aerogel. 30

35 21. A process according to claim 9 substantially as hereinbefore described with reference to any of the foregoing specific examples I to VI. 35

40 22. A silica aerogel whenever prepared or produced by any of the processes hereinbefore described and claimed. 40

45 23. A composition comprising an organic liquid and an amount, sufficient to increase the viscosity of said liquid, of a finely divided amorphous organo-silica aerogel as defined in any of the foregoing claims 1—8 and 22. 45

50 24. A composition according to claim 23 which contains from 0.2% to 5.0% by weight, based on the weight of the composition, of said aerogel. 50

55 25. A composition according to claim 23 or 24 wherein the organic liquid is a solution of an organic high molecular weight film forming compound dissolved in an organic solvent. 55

60 26. A composition according to claim 23 or 24 wherein the organic liquid is a plastisol comprising halogenated vinyl or vinylidene polymer suspended in a liquid plasticizer for said polymer. 60

65 27. A composition according to claim 23 or 24 wherein the organic liquid is an organic solvent having dissolved therein an unsaturated solid alkyd resin of a polyhydroxy alcohol and an unsaturated polycarboxylic acid, said solvent being polymerizable with said resin.

28. A composition according to claim 23 or 24 wherein the organic liquid is a polymerizable liquid comprising an unsaturated alkyd resin obtained by the esterification of a mixture of ingredients comprising a polyhydric alcohol and an alpha-unsaturated, alpha, beta-carboxylic acid. 5

29. A composition comprising (1) a liquid plastisol comprising a polyvinyl halide polymer suspended in a liquid plasticizer and (2) from 0.2% to 3% by weight based on the weight of the composition of a finely divided, amorphous organo-silica aerogel comprising a silica polymer having siloxy groups and containing from 0.4% to 1.2% by weight of carbon and from 0.9% to 1.5% by weight of hydrogen chemically bound to a portion of the siloxy groups, said organo-silica aerogel being further characterized in having an SiO₂ to carbon atom ratio of from 10:1 to 50:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 2:1, said organo-silica aerogel being further characterized in having a total surface area of from 100 to 400 square meters per gram, an external surface area of from 1.70 to 1.95 square meters per gram and an average particle size of from 1.0 to 2.5 microns. 10 10

30. A composition as in claim 29 wherein the finely divided, amorphous, organo-silica aerogel is an organo-silica aerogel comprising a silica polymer having siloxy groups and containing from 0.9% to 1.2% by weight of carbon and from 1.2% to 15 15 1.5% by weight of hydrogen chemically bound to a portion of the siloxy groups, said organo-silica aerogel being further characterized in having an SiO₂ to carbon atom ratio of from 10:1 to 25:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 1.3:1. 20 20

31. A composition as in claim 30 wherein the liquid plastisol comprises a vinyl chloride polymer suspended in diethyl phthalate.

32. A composition comprising (1) a polymerizable liquid comprising an unsaturated solid polyester resin of a polyhydroxy alcohol and an unsaturated polycarboxylic acid dissolved in an organic solvent and (2) an amount sufficient to render said composition thixotropic of a finely divided, amorphous organo-silica aerogel comprising a silica polymer having siloxy groups and containing from 0.4% to 1.2% by weight of carbon and 0.9% to 1.5% by weight of hydrogen chemically bound to a portion of the siloxy groups in said aerogel and having an SiO₂ to carbon atom ratio of from 10:1 to 50:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 2:1, said organo-silica aerogel being characterized in having a total surface area of from 100 to 400 square meters per gram, an external surface area of from 1.70 to 1.95 square meters per gram and an average particle size in the range of from 1.0 to 2.5 microns. 25 25 30

33. A composition comprising (1) a polymerizable liquid comprising an unsaturated solid polyester resin of a polyhydroxy alcohol and an unsaturated polycarboxylic acid dissolved in styrene and (2) from 0.5% to 5.0% by weight, based on the weight of the composition, of a finely divided, amorphous organo-silica aerogel comprising a silica polymer having siloxy groups and containing from 0.4% to 0.8% by weight of carbon and 0.9% to 1.2% by weight of hydrogen chemically bound to a portion of the siloxy groups in said aerogel and having an SiO₂ to carbon atom ratio of from 25:1 to 50:1 and an SiO₂ to hydrogen atom ratio of from 1.3:1 to 2:1, said organo-silica aerogel being characterized in having a total specific surface area of from 100 to 400 square meters per gram, an external surface area of from 1.70 to 1.95 square meters per gram and an average particle size in the range of from 1.0 to 2.5 microns. 35 35 40 40

34. A composition according to claim 33 wherein the polymerizable liquid comprises a solution in styrene of an unsaturated solid polyester resin formed by the reaction of a 25% molar excess of propylene glycol with a mixture of equal mol percentages of maleic anhydride and phthalic anhydride and having no excess of propylene glycol. 45 45

35. A composition comprising (1) a polymerizable liquid comprising a liquid unsaturated alkyd resin obtained by the esterification of a mixture comprising a polyhydric alcohol and an alpha unsaturated alpha, beta polycarboxylic acid and (2) from 0.5% to 5.0% by weight, based on the weight of the composition, of a finely divided, amorphous organo-silica aerogel comprising a silica polymer having siloxy groups and containing from 0.4% to 1.2% by weight of carbon and from 0.9% to 1.5% by weight of hydrogen chemically bound to a portion of the siloxy groups in said aerogel and having an SiO₂ to carbon atom ratio of from 10:1 to 50:1 and an SiO₂ to hydrogen atom ratio of from 0.77:1 to 2:1, said organo-silica aerogel being further characterized in having a total surface area of from 100 to 400 square meters per gram, an external surface area of from 1.70 to 1.95 square meters per gram and an average particle size in the range of from 1.0 to 2.5 microns. 50 50 55 55

36. A composition according to claim 35 wherein the polymerizable liquid is a liquid unsaturated alkyd resin obtained by the esterification of a mixture comprising a 60 60

polyhydric alcohol and an alpha unsaturated alpha, beta polycarboxylic acid and an ester of a monohydric alcohol and an unsaturated polycarboxylic acid capable of copolymerizing with said unsaturated alkyd resin.

5 37. A composition according to claim 35 wherein the polymerizable liquid comprises liquid diethylene glycol maleate obtained by the esterification of a mixture comprising diethylene glycol, maleic anhydride, and a polymerizable ester of an unsaturated monohydric alcohol and polycarboxylic acid.

10 38. A composition comprising (1) a polymerizable liquid consisting essentially of
a liquid unsaturated alkyd resin obtained by the esterification of a mixture comprising
a polyhydric alcohol and an alpha unsaturated alpha, beta polycarboxylic acid and
(2) from 0.5% to 5.0% by weight, based on the weight of the polymerizable liquid, of
an amorphous, finely divided organo-silica aerogel comprising a silica polymer having
siloxyl groups and containing from 0.4% to 0.8% by weight of carbon and from 0.9%
to 1.2% by weight of hydrogen chemically bound to a portion of the siloxyl groups in
said aerogel and having an SiO_2 to carbon atom ratio of from 25:1 to 50:1 and an
 SiO_2 to hydrogen atom ratio of from 1.3:1 to 2:1, said organo-silica aerogel being
further characterized in having a total surface area of from 100 to 400 square meters
per gram, an external surface area of from 1.70 to 1.95 square meters per gram and an
average particle size in the range of from 1.0 to 2.5 microns.

20 39. A composition comprising (1) a oleaginous liquid and (2) an amount sufficient
to thicken said liquid of an amorphous finely divided organo-silica aerogel comprising
a silica polymer having siloxy groups and containing from 0.4% to 1.2% by weight of
carbon and from 0.9% to 1.5% by weight of hydrogen chemically bound to a portion
of the siloxy groups in said aerogel and having an SiO_2 to carbon atom ratio of from
10:1 to 50:1 and an SiO_2 to hydrogen atom ratio of from 0.77:1 to 2:1, said organo-
silica aerogel being further characterized in having a total surface area of from 100
25 to 400 square meters per gram, an external surface area of from 1.70 to 1.95 square
meters per gram and an average particle size in the range of from 1.0 to 2.5 microns.

40. A composition as in claim 39 wherein the oleaginous liquid is a hydrocarbon lubricating oil and said organo-silica aerogel is employed in an amount sufficient to thicken said oil to a grease consistency.

41. A composition according to claim 23 substantially as hereinbefore described with reference to any of the foregoing specific examples VII to XI.

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